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Excess Molar Enthalpies of Acetylene Tetrachloride with Furan, Methylfuran, Tetrahydrofuran and 1,4-dioxane at the Temperature 308.15K

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Abstract

The excess molar enthalpies H^E of mixtures of acetylene tetrachloride with furan or methylfuran or tetrahydrofuran or 1,4-dioxane have been measured over the entire composition range at the temperature Ts 308.15 K. The H^E values are negative for all the mixtures over the whole composition range. The values for n-donor compounds increase in the order furan < methylfuran < 1,4-dioxane< tetrahydrofuran . The H^E values have been used to calculate the excess partial molar enthalpies of the respective components.

Keywords: Microcalorimeter, enthalpy of mixing, acetylene tetrachloride, tetrahydrofuran, furan and specific interaction.

1. INTRODUCTION

The study of acetylene tetrachloride, furan,methyl furan, tetrahydrofuran (Tetrahydrofuran (THF) is an organic compound having the formula $(CH_2)_4O$, which is classified as heterocyclic compound) and 1,4-dioxane, is of interest not only because the compounds are of industrial importance but also because their interactions are pronounced, making them better solvents and also useful in day-to-day life.

Binary systems of acetylene tetrachloride (ATC) ($CHCl_2$ $CHCl_2$) with n-donor compounds are of considerable interest because of the occurrence of specific interactions in the liquid state. This is caused by the presence of four Cl atoms and two H atoms in $CHCl_2$ $CHCl_2$, which can thus act as σ-acceptors toward and be involved in the formation of hydrogen bonds with furan,methyl furan, tetrahydrofuran and 1,4-dioxane($C_4H_8O_2$) . The latter compounds will act as n-donors. These systems were selected to find out the effect of the substitution of the alkyl group in furan (methyl furan) and to establish the effect of one oxygen (tetrahydrofuran) or two oxygens (dioxane) in the cyclic ethers. A literature survey revealed that widespread studies on such systems have not been carried out to date. Recently we have reported data on excess molar enthalpies of dichloromethane with acetone or + dimethyl sulfoxide or + tetrahydrofuran or + 1, 4-dioxane at the temperature 313.15 K[1]. In the present study we report the excess molar enthalpies of acetylene tetrachloride, furan, methyl furan, tetrahydrofuran and 1,4-dioxane over the whole composition range at the temperature 308.15 K. The H^E values have been used to calculate the excess partial molar enthalpies of the respective components. The results, thus obtained have been repored and interpreted in this paper.

2. EXPERIMENTAL SECTION

Acetylene tetrachlorides, furan (BDH, AR), methyl furan (SD Chemicals Analar) were further purified by fractional distillation, and the constant middle fraction was used for the experiments.

1,4-Dioxane (Fluka) and Tetrahydrofuran (E. Merck) was used without further purification. All compounds were dried over freshly activated molecular sieves. Purities of chemicals used are > 99.6 % as determined from GLC.

3. METHOD

A heat flux micro calorimeter (C-80 model supplied from Setaram, France) was used for taking measurements on excess molar enthalpies, H^E, the temperature was restricted within ±0.001K. Preparation of the solutions was done by mass. Accuracy of mole fractions is ±0.0001. The trustworthiness of the instrument was earlier checked by measuring H^E for systems of cyclohexane + hexane at T=298.15 K as given elsewhere. At equimolar composition i.e.at x_1=0.5, the deviation of present work is 0.5% whereas about 1% in the mean deviations of the excess enthalpy is estimated.

4. PROCEDURE

Experiments have been done by batch method on C-80 calorimeter [2]; the calorimeter consists of a reference and experimental vessel. These are surrounded by two symmetrical thermal flux meters composed of thermocouples in series. The whole assembly is kept in an aluminium block and allowed to reach thermal equilibrium. If there is any heat liberated or absorbed in the experimental vessel during mixing of binary mixtures, it leads to change in temperature which is allowed and this persists till same temperature is attained in both the vessels. The experimental cell has two chambers separated by tilting lid. The samples are separately introduced into the vessel by equilibrium. The mixing is performed by inverting the whole calorimeter by 180^0C. The amount of heat, q evolved during an experiment can be calculated by determining the area under the curve obtained during the experiment. The mole fraction of component 1, having weight $w1$ is calculated by using the following relation:

$$x1 = \frac{n1}{n1 + n2}$$

Where $n1 = \frac{w1}{Mol.wt}$ and $n2 = \frac{w2}{Mol.wt}$

$w2$ is the weight of second component.

5. RESULTS AND DISCUSSIONS

Enthalpies of mixing of ATC (1) with furan, methylfuran, THF, or 1,4-dioxane (2) are given in Table 1. The data were fitted to the least squares equation

$$\frac{H^E}{J.mol^{-1}} = x_1 x_2 \sum_{i=0}^{m} A_i\,(x_1 - x_2)^i \qquad (1)$$

where x_1 refers to the mole fraction of $CHCl_2.CHCl_2$. The least square parameters Ai, along with the standard deviation of the fit, σ , are reported in Table 2. The standard deviation of the fit, σ , are calculated using equation

$$\sigma = \left[\frac{\Sigma\left(H^E - H^E_{calc}\right)^2}{(m-n)}\right]^{1/2} \qquad (2)$$

The plots of enthalpies of mixing as a function of the mole fraction x_1 of ATC are given in Fig. 1. All the systems are exothermic in nature, and the electronic environment around the oxygen atom showed a marked effect on the enthalpies of mixing.

Table1: Excess Molar Enthalpies of acetylene tetrachloride ($CH.Cl_2CH.Cl_2$) (1) + furan (2), or + methyl furan (2), or + tetrahydrofuran (2), or + 1,4-dioxane (2) at 308.15 K

$CH.Cl_2CH.Cl_2$ (1) + Furan (2)	
X_1	H^E ($J.mol^{-1}$)
0.0124	-17
0.2231	-167
0.3211	-201
0.4258	-222
0.5166	-229
0.6089	-215
0.7654	-144
0.8663	-95
0.9312	-48
0.9788	-15

$CH.Cl_2CH.Cl_2$ (1) + Methyl Furan (2)	
X_1	H^E ($J.mol^{-1}$)
0.0676	-69
0.1334	-137
0.2112	-239
0.2675	-299
0.3245	-365
0.4678	-485
0.5123	-499
0.5554	-499
0.6676	-465
0.7145	-435
0.7899	-334
0.8221	-295
0.8632	-224
0.9882	-21

$CH.Cl_2CH.Cl_2$ (1) + Tetrahydrofuran (2)	
X_1	H^E ($J.mol^{-1}$)
0.0567	-667
0.1245	-1347
0.1346	-1439
0.2456	-2287
0.3044	-2620
0.3478	-2811
0.4652	-3075
0.5123	-3092
0.5421	-3059
0.689	-2527
0.7243	-2311
0.7667	-2009
0.8765	-1084
0.9764	-193

$CH.Cl_2CH.Cl_2$ (1) + 1,4-Dioxane (2)	
X_1	H^E ($J.mol^{-1}$)
0.0876	-735
0.1165	-959
0.1543	-1237
0.1998	-1550
0.2265	-1720
0.2435	-1824
0.3133	-2199
0.3557	-2375
0.4778	-2710
0.5012	-2732
0.5453	-2738
0.6887	-2393
0.7115	-2287
0.7653	-1984
0.8123	-1662
0.8865	-1060
0.9012	-929
0.9678	-309

The excess enthalpy results from the disruption of interactions between like molecules and the introduction of new interactions between unlike molecules. The partial excess enthalpies $H^{E}_{m,1}$,and $H^{E}_{m,2}$ were calculated from H^E data by using the equation

$$H^{E}_{m,1} = H^E/x_1 + x_{1.}\ x_2[\ \partial(\ H^E/x_1\ )/\ \partial\ x_1]_{p,T} \qquad (3)$$

$$H^{E}_{m,2} = H^E/_{.}\ x_2 + x_{1.}\ x_2[\ \partial(\ H^E/\ x_2\ )/\ \partial\ x_2]_{p,T} \qquad (4)$$

The excess partial molar enthalpies calculated from equation 3 and 4 are plotted in figure 2 and figure 3. The excess partial molar enthalpies are indicative of the type of effects dominating the overall behaviour of excess enthalpy in binary liquid mixtures. The choices of the number of fitting constants in Eq 2 are mainly responsible for the calculation of partial molar enthalpies.

Table 2: Least Squares Coefficients of Eq 1 for the Excess Molar Enthalpies, and the standard deviations, of $CHCl_2CHCl_2$+furan or methyl furan or +tetrahydrofuran or ,+1,4-dioxane at 308.15K

System	**A0**	**A1**	**A2**	**A3**	**σ($Jmol^{-1}$)**
$CHCl_2CHCl_2$+furan	-906.7	62.54	29.56	151	3.8
$CHCl_2CHCl_2$+ methylfuran	-1980	670.2	767	367.3	4.0
$CHCl_2CHCl_2$+ tetrahydrofuran	-12370	494	2076	1876	3.3
$CHCl_2CHCl_2$+1,4-dioxane	-10920	-1431	1678	1075	2.1

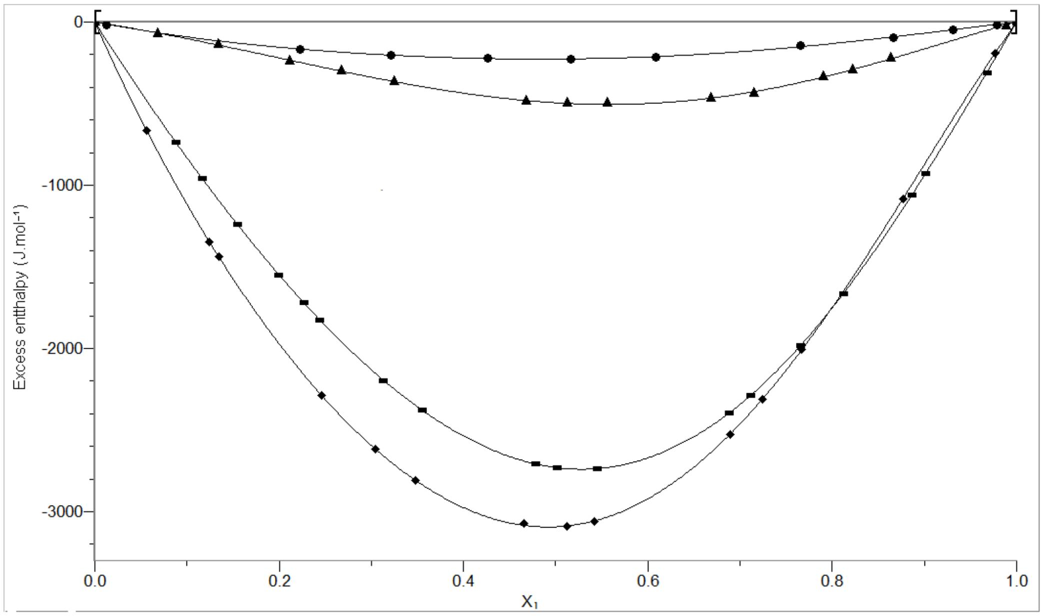

Figure 1: Excess Molar Enthalpies of Acetylene tetrachloride ($CHCl_2CHCl_2$) (1) + furan (2) (●), or + methyl furan (2)(▲), or + tetrahydrofuran (2) (◆), or + 1,4-dioxane (2) (▬) at 308.15 K

The excess enthalpy results from the disruption of interactions between like molecules and the introduction of new interactions between unlike molecules. The magnitude of excess enthalpy of mixing for the present mixtures is attributed to the net result of positive and negative contributions due to breaking of bonds or interactions between similar molecules, and from the formation of new bonds such as hydrogen bonds between dissimilar molecules. The negative values of H^E indicate that the interactions between like molecules are weaker in comparision to unlike molecules in the pure liquids.

The enthalpy of mixing of furan is small, ~ - 230 J mol^{-1} at the minimum, indicating only slight specific interaction between the furan and ATC molecules. The ether oxygen is a weak proton acceptor and can interact to form a hydrogen bond with a proton donor molecule.

However, owing to the presence of two double bonds in the ring, the oxygen becomes less basic, and therefore the possibility of hydrogen bonding is much reduced. The enthalpy of mixing of methylfuran is a little higher than that of furan (H_{min} x = - 400 J mol^{-1}).

This is attributed to an increase in the basic character of the ether oxygen owing to the presence of an electron donor methyl group at the s-carbon atom. The effect of saturation of the furan ring is marked and the THF-ATC system is highly exothermic (H_{min}=-3100Jmol^{-1}). The enthalpies of mixing of 1,4-dioxane is also highly negative. The highly exothermic mixing of these systems indicates strong specific interactions involving the hetero- molecules.

In these systems, two types of interactions are expected. First, the hydrogen bonding between the hydrogen of ATC and the keto or ether oxygen. Hydrogen bonded complex formation of chloroform with tetrahydrofuran and dioxane has been reported in the literature [3,4]. In the present systems the interactions are more complicated than those with chloroform, as ATC (A) has two equivalent proton donors and can thus form AB and A_2 types of complexes with THF (B). In the case of dioxane, it can form AB, A_2B and AB_2 types of complexes.

It may be noted that the minimum heats of mixing for these two systems show the trend: THF > > 1,4-dioxane. In the case of binary hydrogen bond forming systems the number of H-bonds formed, the enthalpy of H-bond formation and other specific interactions are the chief contributors to the enthalpy of mixing. As far as hydrogen bond formation is concerned, dioxane can form more numerous H-bonded species than THF owing to the presence of two oxygens.

So from the viewpoint of H-bond formation the 1,4-dioxane system should be more exothermic than the THF system, but the reverse is observed. Wilhelm et al. [5,6] studied the heats of mixing of carboxylic acids with THF and 1,4-dioxane and found the same trend of interaction. This indicates that the interactions other than H-bonding contribute significantly to the enthalpies of mixing of these systems.

Dincer and Van Ness [7,8] determined the enthalpies of mixing of dichlo romethane with THF and 1,4-dioxane. Both the systems were exothermic and the maximum enthalpy changes were -1343 and -1080J.mol^{-1}. In the case of tetra-chloro systems, the maximum enthalpy changes are nearly twice that of dichloro systems. This clearly indicates that the chlorine atom makes a significant contribution to the energy of interaction.

Williamson and co-workers [9, 10] investigated the ether + CCI_4, ether + $CHC1_3$ and ether + CH_2C1_2systems and quantified the relative strengths of O- H and O- CI interactions. Considering the fact that the small electronegativity difference (0.5) between O and C1 leads to specific interactions, there is a strong possibility of hydrogen bond-type specific interaction between the hydrogen of cyclic ether and the C1 of TCE.

Figures 2 and 3 show the values of excess partial enthalpies which support the above-mentioned predictions.
The excess partial molar enthalpy is known to provide the information about the difference between the enthalpy of molecule in solution and the enthalpy in the pure liquid state.

The negative values of H^Em,1, and H^Em,2 values are evidently due to the presence of strong hydrogen bonds between H atom of $CHCl_2CHCl_2$ and lone pair electrons on the oxygen atom of n-donor compounds as suggested by Tripathi [2] between dibromomethane and acetone. There is also possibility of formation of complex between Cl atom of $CHCl_2CHCl_2$ and lone pairs electrons on Oxygen atom of furan, methylfuran, tetrahydrofuran or 1,4-dioxane.

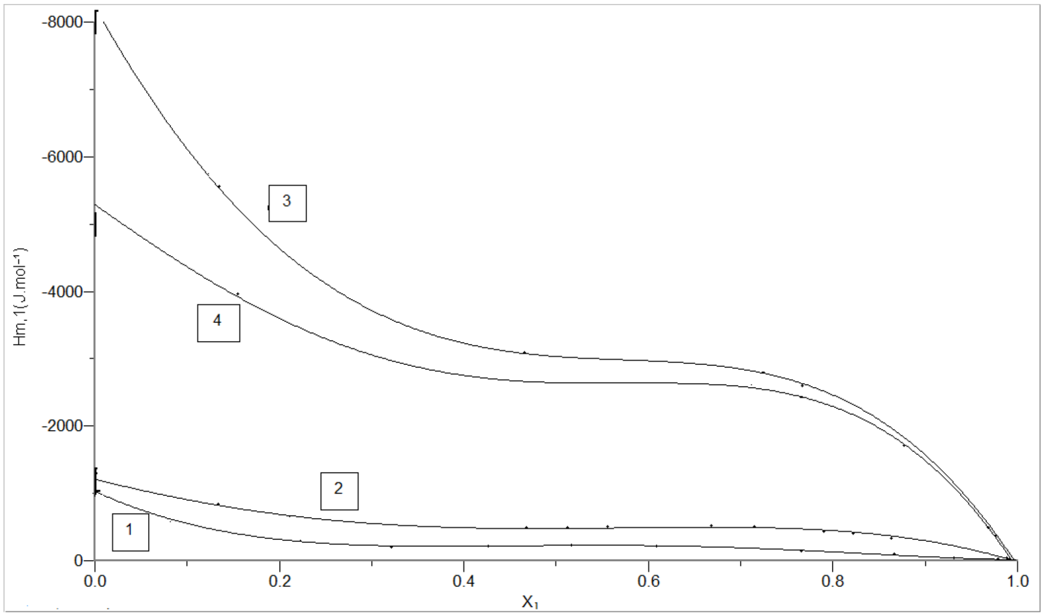

Figure 2: Partial molar Excess enthalpies Hm,1 of binary liquid mixtures of x1 acetylene tetrachloride + x2furan (1), + x2methyl furan (2) , + x2 tetrahydrofuran (3),+ x2 1,4-dioxane(4) at 308.15K.

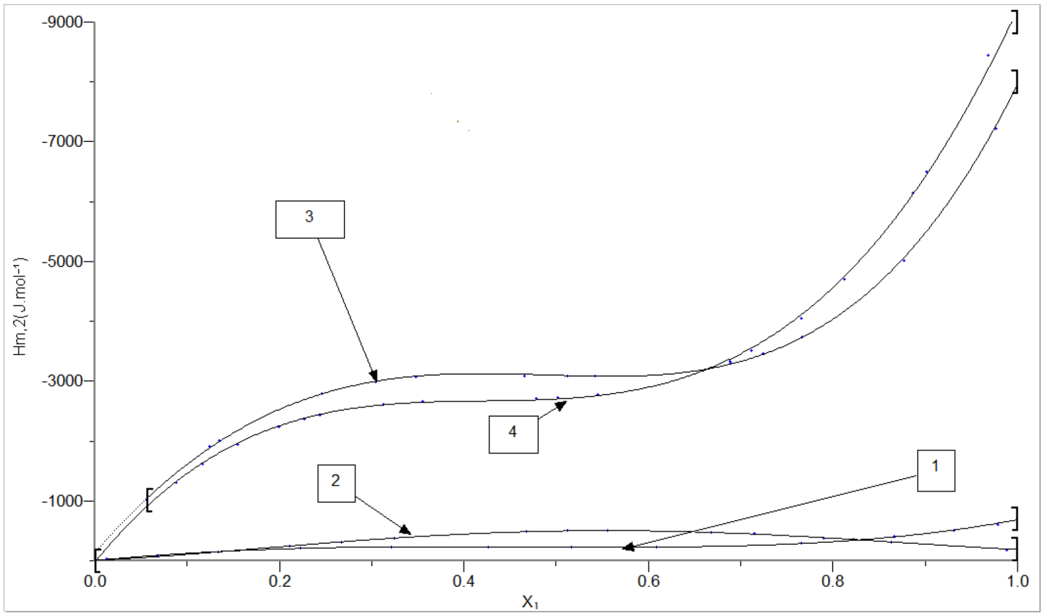

Figure 3: Partial molar Excess enthalpies Hm,2 of binary liquid mixtures of x1 acetylene tetrachloride + x2 furan (1), + x2methyl furan (2) , + x2tetrahydrofuran(3),+ x2 1,4-dioxane (4) at 308.15K.

6. CONCLUSIONS

The interactions between cyclic ethers or ketones and chloro compounds are governed essentially by the saturation or unsaturation of the ring. When the ring is unsaturated, the interactions are weak and substitution of a methyl group at the α-carbon atom enhances the interactions. For cyclic ethers with a saturated ring, the interactions become many times stronger. In these systems not only the O... H and O--C1 interactions [10] but interactions between CH_2 groups and chlorine atoms contribute to the enthalpies of mixing. The interaction of

TCE with aliphatic ketones is much stronger than with aliphatic ethers [11]. However, in the case of cyclic ether, the interactions of hydrogen and chlorine atoms are so dominant that the presence of a functional group or the position of oxygen within or external to the ring does not make any significant difference to the enthalpy of mixing.

7. ACKNOWLEDGMENT

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